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A Study of the Dissolution of Pyrolusite in Sulphuric Acid

John J. Worsdell

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A Study of the Dissolution
of Pyrolusite in Sulphuric Acid

By

John J. Worsdell

Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
MAY, 1942

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C O N T E N T S

INTRODUCTION	1
T E S T I N G P R O C E D U R E	3
T E S T S	4
CONDENSED FORM OF TESTS AND SOLUBILITIES . . .	17
R E S U L T S O F T E S T S	18
C O N C L U S I O N S	19
B I B L I O G R A P H Y	24
A C K N O W L E D G E M E N T S	25

I L L U S T R A T I O N S

PLATE I	21
PLATE II	22
PLATE III	23

INTRODUCTION

With an eye to the future development of its resources, the large deposits of low-grade manganese ore within Montana's boundaries show great promise of developing an important industry. With the present war demands and the possibility of a future market it is essential that work be expended to utilize this important mineral.

One possible and probable method for recovering the manganese is by electrolytic deposition. Power developed by the Grand Coulee Dam in the state of Washington, or some future electric plant in this state itself, should make power available to such plants in sufficient quantities. With these two important factors- large amounts of manganese and sufficient power- present, the hydrometallurgy of manganese in Montana should be an imminent possibility in the near future.

There is in operation at the present time a commercial electrolytic plant for the recovery of manganese from pyrolusite. It is located at Knoxville, Tennessee, and is operated by the Electro Manganese Corp.

This plant does not make public all of the information concerning its process and it is not possible to know if their method would be applicable to the Montana ores until a further study is made.

The Tennessee plant literature reveals that they treat the same mineral of which Montana has large low-grade deposits. They roast the ore to MnO , using producer gas, and then cool the material to below $100^{\circ} C.$ in the absence of air. This furnacing at $760^{\circ} C.$ is done prior to leaching the ore in sulphuric acid. A good solubility of the ore is accomplished by this method. Aside from this information about the process, the conditions of it's operations are not given.

The preceding discussion has shown the desirability for an investigation of the hydrometallurgy of manganese. As the first step a study of the dissolution of pyrolusite in sulphuric acid has been made, the results and conclusions being submitted in this paper.

The United States Bureau of Mines^{1&2} has made investigations relative to the dissolution of various manganese ores in solutions of SO_2 . The results of their tests show that the manganese was dissolved rapidly from pyrolusite by agitation with a 2 per cent SO_2 solution at room temperature. No heating or reducing operations had been made on the ore prior to leaching. This information should be of great help in the investigation of the dissolution of the Phillipsburg pyrolusite in sulphuric acid. It should be borne in mind, however, that H_2SO_4 is generated in the electrolytic cells and consequently will be used at the major solvent, hence the leachability of these ores in H_2SO_4 must be determined.

TESTING PROCEDURE

The testing was performed on MnO_2 obtained in the laboratory and an ore from Phillipsburg, Montana, assaying 29.8 % manganese.

A standard procedure was followed in the leaching tests. The material to be tested was placed in a bottle with 250 cubic centimeters of 10 % sulphuric acid and agitated on rollers for 18 and 24 hour periods. After this, the residue of the leach was filtered from the solution, dried, weighed, and assayed for manganese by the Volhard method.

The heating was done with a gas muffle furnace (Plate I & II), the charge being placed in the muffle in an evaporating dish. The temperatures were taken by means of an optical pyrometer.

Reducing was done in the electric furnace by passing a stream of natural gas through the furnace over the charge (Plate III). The reducing atmosphere was maintained through the subsequent cooling period by continuing the passage of natural gas over the charge until room temperature was reached.

TEST NO. 1

The shelf MnO_2 was tested for its solubility in various strengths of sulphuric acid. The material was leached in 10 % and 20 % (by weight) solutions of sulphuric acid.

The operation was done by agitating the pyrolusite and sulphuric acid together in bottles as previously described.

MATERIAL TESTED: - Shelf MnO_2 (-100 mesh)

FURNACE CONDITIONS: - No heating.

LEACHING CONDITIONS: - Two leaches of 10 % and 20 % sulphuric acid; agitation in bottles by means of rollers for twenty four hours.

MANGANESE DISSOLVED: - 13.9 % in 10 % H_2SO_4

13.0 % in 20 % H_2SO_4

TEST NO. 2

The low solubility of manganese in Test No. 1 suggested that some additional treatment be given the pyrolusite before leaching; and therefore heating the material was tried.

For this test the material was heated in the gas furnace for two hours at an average temperature of 454° C. There was no change in the color of the pyrolusite during the heating period.

MATERIAL TESTED: - Shelf MnO_2 (-100 mesh)

FURNACE CONDITIONS: - Heated two hours in gas muffle furnace at an average temperature of 454° C.

LEACHING CONDITIONS: - Leached in ten per cent sulphuric acid for twenty four hours and agitated in bottles by means of rollers. Ten grams of the furnaced material were placed in the bottle with 250 cubic centimeters of the acid.

MANGANESE DISSOLVED: - 6.8 %

The very small amount of manganese dissolved in Test No. 2 revealed that heating the MnO_2 at 454° C. for 2 hours had no favorable effect on the solubility.

TEST NO. 3

In test No. 3 a higher temperature for the furnacing operation was tried to find its effect on the solubility of the manganese. This trial is similar to the previous test in every respect except for the furnace temperature and the length of the heating period.

On removal from the furnace it was found that the color of the pyrolusite had changed from black to brown.

MATERIAL TESTED: - Shelf MnO_2 (-100 mesh)

FURNACE CONDITIONS: - Heated for 1 hour in the gas muffle furnace at an average temperature of 906°C .

LEACHING CONDITIONS: - Leached in ten per cent sulphuric acid for twenty four hours and agitated in bottles on rollers. The charge was ten grams of furnaced material in the bottle with 250 cubic centimeters of the acid.

MANGANESE DISSOLVED: - 15.0 %

Heating the pyrolusite at 906°C . for an hour did not increase its solubility in sulphuric acid materially.

TEST NO. 4

In Test No. 4 the material was heated for two hours at approximately the same temperature to determine if the longer heating period would improve its solubility.

The black pyrolusite changed to a brown color during the heating period of two hours.

MATERIAL TESTED: - Shelf MnO_2 (-100 mesh)

FURNACE CONDITIONS: - Heated for two hours in gas muffle furnace at an average temperature of 923°C .

LEACHING CONDITIONS: - Leached in ten per cent sulphuric acid for twenty four hours and agitated in bottles on rollers. The charge was ten grams of furnaced material in the bottle with 250 cubic centimeters of the acid.

MANGANESE DISSOLVED: - 16.5 %

Heating the material for a longer period of time failed to improve the solubility of the manganese.

TEST NO. 5

It became evident in Test No. 4 that heating the pyrolusite would not improve the solubility of the manganese, but one more test at a higher temperature was made to verify this belief.

The pyrolusite was heated for one hour at an average temperature of 1063° C. It changed physically from a black granular material to a hard brown cake during the furnace operation.

MATERIAL TESTED: - Shelf MnO_2 (-100 mesh)

FURNACE CONDITIONS: - Heated for one hour in the gas muffle furnace at an average temperature of 1063° C.

LEACHING CONDITIONS: - Leached in ten per cent sulphuric acid for twenty four hours and agitated in bottles on rollers. The charge was ten grams of furnaced material in the bottle with 250 cubic centimeters of the acid.

MANGANESE DISSOLVED: - 18.3 %

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TEST NO. 6

The results of the four heating tests made on the shelf pyrolusite show no improvement in the solubility of manganese; therefore some other form of treatment must be made on the material other than that of straight heating.

Heating the material under reducing conditions was done in Test No. 6. This was performed by leading a stream of natural gas into the muffle through a quarter inch pipe. The reducing atmosphere was maintained with the gas while the charge cooled down after the heating period. The color of the pyrolusite did not change during this operation.

MATERIAL TESTED: - Shelf MnO_2 (-100 mesh)

FURNACE CONDITIONS: - Heated for one hour at an average temperature of 1027°C . under reducing conditions.

LEACHING CONDITIONS: - Leached in ten per cent sulphuric acid for twenty four hours and agitated in bottles on rollers. The charge was ten grams of the reduced material in the bottle with 250 cubic centimeters of the acid.

TEST NO. 6 (Cont'd)

MANGANESE DISSOLVED: - 67.4 %

Heating the pyrolusite under reducing conditions greatly improved the solubility of the manganese in sulphuric acid.

TEST NO. 7

As the previous test was conducted in the gas muffle furnace where the admission of air could not be entirely eliminated, another test was run in the electric furnace which gave better conditions for reducing.

Metal boats containing the pyrolusite were placed in the electric furnace and heated at 700° C. for one hour in a reducing atmosphere.

The pyrolusite was converted to a brown material during the operation.

MATERIAL TESTED: - Shelf MnO_2 (-100 mesh)

FURNACE CONDITIONS: - Heated for one hour at 7000 C. under reducing conditions.

LEACHING CONDITIONS: - Leached in ten per cent sulphuric acid for twenty four hours and agitated in bottles on rollers. The charge was ten grams of the reduced material in the bottle with 250 cubic centimeters of the acid.

MANCANESE DISSOLVED: - 80.55 %

TEST NO. 8

It is clearly shown that by reducing pyrolusite the solubility of the manganese has been greatly improved. However further tests were made to find out if complete solubility could be obtained. The investigations of the U.S.B.M. revealed that SO_2 solution was a good solvent for manganese, so it was decided to try it in Test No. 8.

The SO_2 was added to the leaching solution by bubbling the gas through the mixture of reduced material and acid.

MATERIAL TESTED: - Reduced material from Test No. 7.

LEACHING CONDITIONS: - The charge was ten grams of the reduced material in ten per cent sulphuric acid. This was agitated on rollers for one hour and then SO_2 was bubbled through the mixture for a few seconds. The agitation was then continued for an additional 17 hours and SO_2 gas was bubbled through the mixture again until the solution was saturated. It was noted that the color of the solution changed from pink to colorless when the gas was introduced.

MANGANESE DISSOLVED: - 98.5 %

TEST NO. 9

The previous test verified the results published by the U.S.B.M., as a practically complete dissolution of the manganese was obtained in a saturated solution of SO_2 in sulphuric acid.

Having gained familiarity with the procedure of testing for the dissolution of manganese, the writer applied the experiments to the pyrolusite ores from Phillipsburg, Montana. The head samples assayed 29.8 % manganese.

The ore was reduced with natural gas in the electric furnace for one hour at a temperature of 700°C . The product had turned a brown color during the reducing period in the furnace.

MATERIAL TESTED: - Phillipsburg ore (-80 mesh)

FURNACE CONDITIONS: - Heated for 1 hour in electric furnace at 700°C . under reducing conditions.

LEACHING CONDITIONS: - The charge was ten grams of the reduced material in ten per cent sulphuric acid. This was agitated on rollers for one hour and then SO_2 was bubbled through the mixture for a few seconds. The agitation was then continued for an additional 17 hours and SO_2 gas was bubbled through the mixture again until the solution was saturated.

MANGANESE DISSOLVED: - 99.9 %

TEST NO. 10

Leaching the reduced Phillipsburg ore in the presence of SO_2 put practically all of the manganese in solution. This was expected, but the test was run to determine any effects the impurities in the ore might have on the manganese solubility.

The raw Phillipsburg ore, without prior heating or reducing treatments, was leached in ten per cent sulphuric acid to determine the solubility of the manganese.

MATERIAL TESTED: - Phillipsburg ore (-80 mesh)

FURNACE CONDITIONS: - No furnacing or reducing.

LEACHING CONDITIONS: - The charge of ten grams of the untreated ore in 250 cubic centimeters of a ten per cent sulphuric acid was agitated for eighteen hours in a bottle.

MANGANESE DISSOLVED: - 9.12 %

The untreated pyrolusite ore from Phillipsburg gave up little of its manganese to solution when it was leached with ten per cent sulphuric acid.

TEST NO. 11

For Test No. 11 the ore was reduced with natural gas in the electric furnace for one hour at a temperature of 700° C. During the reducing period the pyrolusite ore had changed to a brownish colored material. The gas was kept passing through the furnace during the cooling period to maintain a reducing atmosphere until room temperature was reached.

MATERIAL TESTED: - Phillipsburg ore (-80 mesh)

FURNACE CONDITIONS: - Heated for one hour in the electric furnace at 700° C. under reducing conditions.

LEACHING CONDITIONS: - Leached in ten per cent sulphuric acid for eighteen hours and agitated in bottle on rollers. The charge was ten grams of the reduced ore in the bottle with 250 cubic centimeters of the acid.

MANGANESE DISSOLVED: - 85.0 %

TEST NO. 12

The reduced ore had 85 % of its manganese made soluble in a 10 % sulphuric acid solution while the same ore had practically all its manganese dissolved when the acid had been saturated with SO_2 . From this it is gathered that a certain amount of SO_2 is required to completely dissolve the manganese. In Test No. 12 the amount of SO_2 was not determined, but was merely bubbled through the acid for a few seconds.

MATERIAL TESTED: - Phillipsburg ore (-80 mesh)

FURNACE CONDITIONS: - Heated for one hour in the electric furnace at 700°C . under reducing conditions using natural gas.

LEACHING CONDITIONS: - The charge was ten grams of reduced ore in 250 cubic centimeters of ten per cent sulphuric acid. SO_2 was bubbled through the leaching mixture for a few seconds before agitation was started. Agitation was on rollers for eighteen hours.

MANGANESE DISSOLVED: - 91.7 %

CONDENSED FORM OF TESTS AND SOLUBILITIES

No. Of test.	Furnace Conditions	Time in Furnace	Time of Leach	% Mn dissolved
	SHELF MnO ₂ (-100 mesh)			
1	No furnacing	0	24 hr.	13.9 (10% H ₂ SO ₄) 13.0 (20% H ₂ SO ₄)
2	Heated at 454°C. in gas furnace.	2	24 hr.	6.8
3	Heated at 906°C. in gas furnace	1	24 hr.	15.0
4	Heated at 923°C. in gas furnace	2	24 hr.	16.5
5	Heated at 1063°C. in gas furnace	1	24 hr.	18.3
6	Reduced in gas furnace-1027° C.	1	24 hr.	67.4
7	Reduced in elec. furnace-700° C.	1	24 hr.	80.55
8	Reduced in elec. furnace-700° C.	1	18 hr. SO ₂ (satur)	98.5
	PHILLIPSBURG ORE (-80 mesh)			
9	Reduced in elec. furnace-700° C.	1	18 hr. SO ₂ (Satur)	99.9
10	No furnacing	0	18 hr.	9.12
11	Reduced in elec. furnace-700° C.	1	18 hr. No SO ₂	85.0
12	Reduced in elec. furnace-700° C.	1	18 hr. little SO ₂	91.7

RESULTS OF TESTS

Simple heating of the shelf pyrolusite and of the Phillipsburg ore failed to alter the properties which would make their manganese more soluble in sulphuric acid. Variations in temperature and in time of furnacing did not improve the dissolution in any respect. Therefore it was verified that heating will not improve the solubility of manganese from pyrolusite in sulphuric acid solutions.

Furnacing the ore and the shelf pyrolusite under reducing conditions increased the solubility of the manganese greatly. Eighty-five per cent seems to be about the limit to which manganese is soluble from the reduced ore in the sulphuric acid solutions.

The manganese in the reduced ores is entirely soluble in sulphuric acid that has been saturated with SO_2 gas. However, when the gas is bubbled through the leaching mixture of reduced material and sulphuric acid for only a relatively short time not all of the manganese is dissolved, which fact shows that a certain strength of SO_2 is needed to produced complete solubility.

CONCLUSIONS

As a whole, the tests thus far completed are not sufficient to facilitate the design of a flow sheet for the dissolving of manganese from pyrolusite on a commercial scale. Although complete dissolution was obtained when the leaching solution was saturated with SO_2 gas, the process has not been proved practicable from an economic standpoint as yet.

Between 80 and 85 per cent of the manganese can be dissolved in the sulphuric acid leach from the reduced ore without the use of SO_2 . Further study on this point is suggested by the writer as well as research on the following phases;

1. Tests in which a longer period of reducing is used to determine if more complete dissolution of the manganese could be obtained.

2. Tests on unfurnaced ore using varying amounts of SO_2 in the leaching solutions.

3. If the above suggested tests do not produce satisfactory results, then work on the reduced ore with varying and measured amounts of SO_2 should be tried to learn the concentration with which manganese can be most economically dissolved.

CONCLUSIONS (cont'd)

Of the suggested tests, No. 3 seems to have the best possibilities. By determining the SO_2 concentration at which the best manganese dissolution is obtained in the sulphuric acid leach solution, the amount of gas required to treat a known quantity of ore can be found.

Due to limited time available, this investigation is not complete, but the results obtained indicate that the problem is worthy of more extensive study.



PLATE I

Gas Muffle Furnace for Heating Pyrolusite

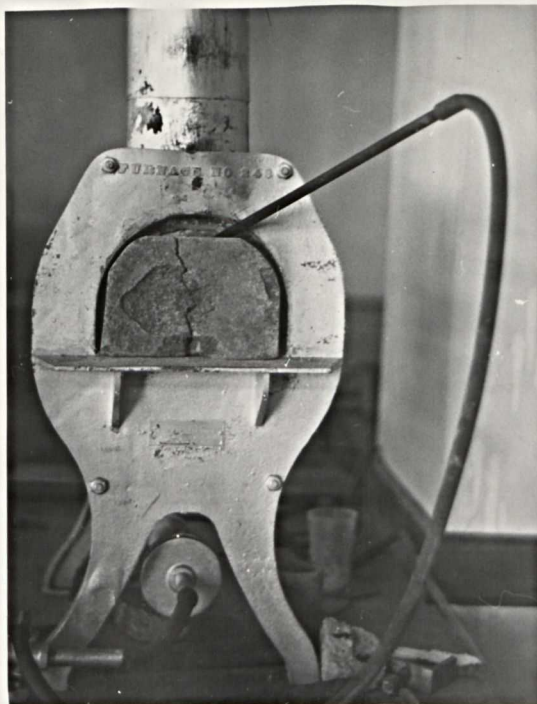


PLATE II

Gas Furnace with Natural Gas Led
into Muffle to Reduce the Pyrolusite



PLATE III

Electric Furnace used
for Reducing Pyrolusite

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